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Title of Invention: Heat transfer fluid

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Inventor: S. Inagaki
c/o Sakai Manufacturing Factories, Metal Plant, Daikin Kogyo K. K.
1304 Kaneoka Cho, Sakai Shi, Osaka Fu
Inventor: N. Kobayashi
c/o Sakai Manufacturing Factories, Metal Plant, Daikin Kogyo K. K.
1304 Kaneoka Cho, Sakai Shi, Osaka Fu
Inventor: S. Uemura
c/o Sakai Manufacturing Factories, Metal Plant, Daikin Kogyo K. K.
1304 Kaneoka Cho, Sakai Shi, Osaka Fu
Inventor: M. Noguchi
c/o Sakai Manufacturing Factories, Metal Plant, Daikin Kogyo K. K.
1304 Kaneoka Cho, Sakai Shi, Osaka Fu
Attorney: E. Mieda, Patent Counsel, and 2 others

## Specification

Title of Invention: Heat transfer fluid

Claims of the Patent

1.Heating medium consisting of the organic compound which is expressed by the molecular formula: $C_3H_mF_n$ (where m = 1 ~ 5, n = 1 ~ 5 and m + n = 6) and has one double bond in the molecular structure.

### Field of Application in Industry

This invention is related to the heat transfer medium that is used in the refrigerating machine, heat pump, etc.

In this specification, "%" means "weight %".

### Existing Technologies and Their Problems

In the past, as for the heating medium (refrigerant) of the heat pump, the chloro fluoro hydrocarbon, fluoro hydrocarbon, the azeotropic composition of them and the composition near them were known. These were commonly called the fleon and, currently, R- 11 (tri chloro mono fluoro methane), R-22 (mono chloro di fluoro methane) and R- 502 (R-22 + chloro penta fluoro ethane), etc. are used mainly.

Recently, however, it has been pointed out that, when discharged into the atmospheric air, the felons of certain types destroy the ozone layer of the stratosphere and, as the result, seriously adverse effects are given to the bio systems on the earth including the human being. Consequently, for the fleons having high danger of destroying the ozone layer, their production and use are to be regulated by an international agreement. The felons that are the object of this regulation include R-11 and R-12 and, as to the R-22, it is currently not included in the object of regulation because its effect on the ozone layer destruction is small but, in future, the appearance of a refrigerant having less influence is being desired. With the spread of refrigerating and air conditioning facilities, the demand for fleon is increasing every year and so the regulation of its production and use would have a very large influence on the whole of current social structure including the residential environment. Therefore, the development of a new heating medium (refrigerant) for use in the heat pump having no or a very small danger of generating the problem of ozone layer destruction is an urgent problem.

## The Means for Solving the Problem

The present inventors have repeatedly conducted various studies to obtain a new heat transfer fluid which is suitable for the heat pump or heat engine that naturally has little or no adverse effect on the ozone layer when discharged into the atmospheric air. As the result, it was found that the organic compound having a specific structure has the conditions meeting the objective.

Thus, this invention provides the heat transfer fluid described below.

[Heat transfer fluid consisting of the organic compound that is expressed by the molecular formula $C_3HmFn$ (where $m = 1 \sim 5$, $n = 1 \sim 5$ and $m + n = 6$) and has one double bond in the molecular structure.]

Major physical properties of the representative compounds that are used in this invention are as follows.

(I.) $F_3C - CH = CH_2$ (3, 3, 3 – tri fluoro -1- propene)

| | |
|---|---|
| Boiling point | -17.0 deg C |
| Critical temperature | 126 deg C |
| Critical pressure | 41 kg / cm2 |
| Molecular weight | 90.65 |

(II.) $F_3C - CH = CHF$ (1, 3, 3, 3 - tetra fluoro -1- propene)

| | |
|---|---|
| Boiling point | -16.0 deg C |
| Critical temperature | 121 deg C |
| Critical pressure | 39.1 kg / cm2 |
| Molecular weight | 114.04 |

(III.) $F_3C - CF = CF_2$ (1, 2, 2 - tri fluoro -1- propene)

| | |
|---|---|
| Boiling point | -18.0 deg C |
| Critical temperature | 121 deg C |
| Critical pressure | 40.9 kg/ cm2 |
| Molecular weight | 69.05 |

(IV.) $H_3C - CF = CH_2$ (2 - mono fluoro -1- propene)

| | |
|---|---|
| Boiling point | -24.0 deg C |
| Critical temperature | 123 deg C |
| Critical pressure | 45.1 kg / cm2 |
| Molecular weight | 60.07 |

The compound expressed by $C_3HmFn$ that is used as the heat transfer fluid in this invention does not at all contain the chlorine atom and bromine atom that gives influence on the ozone layer and, therefore, it does not have the danger of generating the problem of ozone layer destruction.

Also, on the other hand, the compound expressed by $C_3HmFn$ has excellent properties as the heating medium for heat pump and has excellent balance in the performances such as performance factor, refrigeration capability, condensation pressure, discharge temperature, etc. Furthermore, the boiling point of this compound is close to those of R-12, R- 22, R- 114 and R- 502 and, therefore, it is suitable for use under the service conditions of known heating medium, i.e. the evaporation temperature of -20 ~ 10 deg C and the condensation temperature of 30 ~ 60 deg C.

Also, in this invention, one can also use as the heat transfer medium the mixture that contains at least the compound expressed by $C_3HmFn$ and at least one selected from the group consisting of R- 22 ($CHClF_2$), R- 32 ($CH_2F_2$), R- 124 ($CF_3CHClF$), R- 125 ($CF_3CF_2H$), R- 134a ($CF_3$ CFH2, it is possible to improve the refrigeration capacity ), R- 142b ($CH_3CClF_2$), 143a (CF3 CH3), R- 152 (CHF2 CH3). In the case of using this mixture further by mixing a refrigerant of lower boiling point and it is possible to improve the performance factor or improve the solubility with the refrigeration machine oil by mixing the refrigerant of a larger latent heat of evaporation.

For the compound expressed by $C_3HmFn$ or the mixture of the compound expressed by $C_3HmFn$ and at least one of R- 22, R- 32, R- 124, R- 125, R- 134a, R- 142b, R- 143a and R- 152a that is used in this invention, it was confirmed that there is no problem with respect to general properties that are required of the heating medium for the heat pump (e.g. the miscibility with the lubrication oil, non- corrosiveness to the materials, etc.).

Effectiveness of the Invention

By the heat transfer fluid that is due to this invention, the following remarkable effects are achieved.

(1.) Compared with the heat pumps that have been using R- 12, R- 22 or R- 502 as the heating medium from the past, equal or better cyclic performance is obtained.,
(2.) Because of the excellent performance as the heating medium, it is advantageous in the designing of machines.
(3.) Even if the heat transfer fluid of this invention is discharged into the atmospheric air, there is no danger of destroying the ozone layer.

Examples of Application

In the following, examples of application and comparative examples are shown to further clarify the characteristic features of this invention.

Example of Application 1

With a heat pump of 1 horse power that uses as the heating medium F3 C – CH = CH2 (3, 3, 3 – tri fluoro -1- propene), the evaporation temperature of the heating medium at the evaporator was set at -10 deg C, -5 deg C and 10 deg C, and the condensation temperature at the condenser was set at 50 deg C and the degree of superheating and the degree of super-cooling were set at 5 deg C and 3 deg C, respectively, and the operation was conducted.

Also, as the comparative examples, R- 12 (Comparative Example 1), R- 22 (Comparative Example 2) and R- 502 (Comparative Example 3) were used as the heating medium and the operation of heat pump was conducted under the same condition as described above.

From the results of these, the coefficient of performance (COP)) and the refrigeration effect were determined from the following equation (see the Mollier chart shown in Fig. 1).

$COP = (h_1 - h_4)/ (h_2 - h_1)$
Refrigeration effect $= h_1 - h_4$

$h_1$ = Enthalpy of the working fluid at the exit of evaporator
$h_2$ = Enthalpy of the working fluid at the inlet of condenser
$h_4$ = Enthalpy of the working fluid at the inlet of evaporator

The circuit diagram of refrigeration cycle which was used in this example of application and the comparative example is shown in Fig. 2.

The results of calculation of the COP and refrigeration capacity are shown Fig.3 and Fig. 4, respectively, by comparing with the results of Comparative Examples 1 ~ 3.

Also, the coefficient of performance shown in Fig. 3 is the value obtained by dividing the measured value ($COP_A$) of each heating medium by the measured value (COPa) at the evaporation temperature 5 deg C in the case of using R- 22 as the heating medium. In particular, the result of heating medium that is due to this invention is indicated by "O".

Also, the refrigeration capacity shown in Fig. 4 is the value obtained by dividing the measured value of each heating medium (capacity A) with the measured value (capacity B) at the evaporation temperature of 5 deg C in the case of using R- 22 as the heating medium. The result of the heating medium that is due to this invention is again indicated by "O".

As is clear from Fig. 3, the working fluid which is due to this example of application exhibits comparably good value of COP relative to R- 12 and R- 22. Further, as is clear from Fig. 4, it exhibits higher value of refrigeration effect than R- 12.

Also, the results of comparison of condensation pressure and discharge temperature of the compressor at the evaporation temperature of 5 deg C are shown in Table 1.

Table 1

| | Condensation pressure (kg/ cm2. A) | Discharge temperature (deg C) |
|---|---|---|
| Example of Application 1 | 9 | 51 |
| Comparative Example 1 | 12 | 59 |
| Comparative Example 2 | 20 | 73 |
| Comparative Example 3 | 22 | |

The condensation pressure and discharge temperature of the heating medium which is due to this example of application indicate lower values than that of R- 12 and this is advantageous in the designing of equipment.

From the results shown above, it is clear that, in this example where F3 C – CH = CH2 is used as the heating medium, the cycling performance which is better than that of the heat pump which used R- 12, R- 22 and R- 502 that have been used from the past and that this invention is advantageous in the designing of equipment.

Example of Application 2

As the heating medium, F3C – C – CH = CHF (1, 3, 3, 3- tetra fluoro -1- propene) was used and the evaporation temperature of the heating medium at the evaporator was set at 5 deg C. Other than these, the same procedure as in Example of Application 1 was followed to conduct the operation of heat pump.

Coefficient of performance and the refrigeration capacity are shown in Table 2 below. All of the values indicate the numerical value obtained by dividing the measured values ($COP_A$ and refrigeration $capacity_A$) of the heating medium of this invention with the

measured values ($COP_a$ and refrigeration capacity$_a$) at the evaporation temperature of 5 deg C in the case of using R- 22 as the heating medium.

Table 2

| | Example of Application 2 | R- 12 | R- 502 |
|---|---|---|---|
| $COP_A$/ $COP_a$ | 1.01 | 1.02 | 0.92 |
| $Capacity_A$/ $Capacity_a$ | 0.43 | 0.61 | 1.03 |

Example of Application 3

As the heating medium, H3C – C – CF = $CF_2$ (1, 2, 2 - tri fluoro -1- propene) was used and the evaporation temperature of the heating medium at the evaporator was set at 5 deg C. Other than these, the same procedure as in Example of Application 1 was followed to conduct the operation of heat pump.

Coefficient of performance and the refrigeration capacity are shown in Table 3 below. All of the values indicate the numerical value obtained by dividing the measured values ($COP_A$ and refrigeration capacity$_A$) of the heating medium of this invention with the measured values ($COP_a$ and refrigeration capacity$_a$) at the evaporation temperature of 5

Table 3

| | Example of Application 3 | R- 12 | R- 502 |
|---|---|---|---|
| $COP_A$/ $COP_a$ | 1.00 | 1.02 | 0.92 |
| $Capacity_A$/ $Capacity_a$ | 0.44 | 0.61 | 1.03 |

Example of Application 4

As the heating medium, H3C – C – CF = $CH_2$ (2 - mono fluoro -1- propene) was used and the evaporation temperature of the heating medium at the evaporator was set at 5 deg C. Other than these, the same procedure as in Example of Application 1 was followed to conduct the operation of heat pump.

Coefficient of performance and the refrigeration capacity are shown in Table 4 below. All of the values indicate the numerical value obtained by dividing the measured values ($COP_A$ and refrigeration capacity$_A$) of the heating medium of this invention with the measured values ($COP_a$ and refrigeration capacity$_a$) at the evaporation temperature of 5

Table 4

| | Example of Application 4 | R- 12 | R- 502 |
|---|---|---|---|
| $COP_A$/ $COP_a$ | 1.03 | 1.02 | 0.92 |
| $Capacity_A$/ $Capacity_a$ | 0.53 | 0.61 | 1.03 |

Example of Application 5

As the heating medium, F3C – C – CF = $CH_2$ was used. Other than these, the same procedure as in Example of Application 1 was followed to conduct the operation of heat pump and approximately same results as in Example of Application 1 were obtained.

Brief Description of the Figures

Fig. 1 is the Mollier diagram which was used in determining the coefficient of performance (COP) and the refrigeration effect in the example of application.

Fig. 2 is the circuit diagram of the refrigeration cycle which was used in the example of application and the comparative example.

Fig. 3 is the graph showing COPs that are due to Example of Application 1 and Comparative Examples 1 ~ 3.

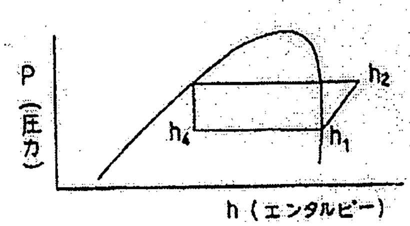
Fig. 4 is the graph showing refrigeration capacity that is due to Example of Application 1 and Comparative Examples 1 ~ 3.

Attorney: E. Mieda, Patent Counsel

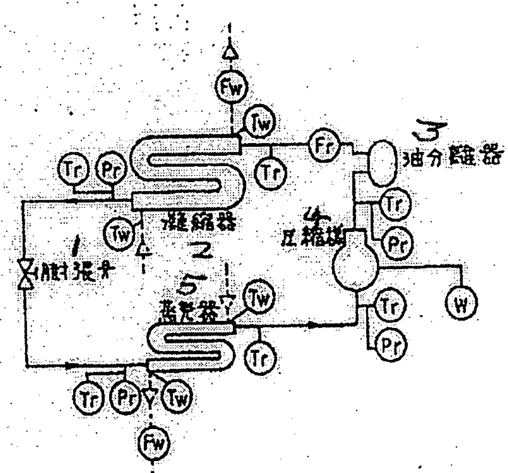
**Figures** (See the figures below with the following indexed translation of the Japanese words appearing in the figures).

1. Expansion valve; 2. Condenser; 3. Oil separator; 4,. Compressor; 5. Evaporator; 6, 7. Evaporation temperature; 8. $Capacity_A$/ $Capacity_B$.
h. Enthalpy; P. Pressure

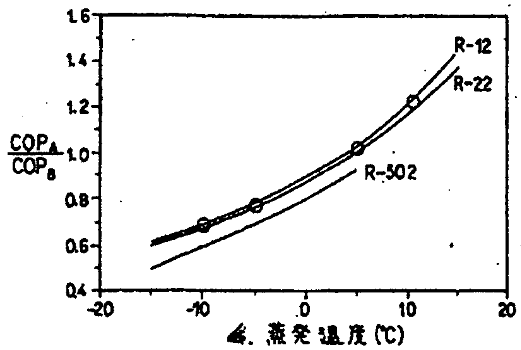
第 1 図



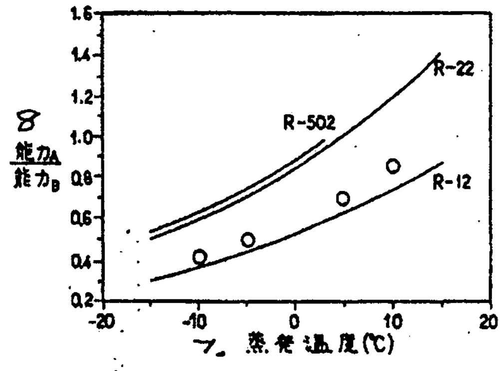

第 2 図



第 3 図


R-12
R-22
R-502
$\frac{COP_A}{COP_B}$
1.6
1.4
1.2
1.0
0.8
0.6
0.4
-20
-10
0
10
20
蒸発温度(℃)

第 4 図


R-22
R-502
R-12
$\frac{能力_A}{能力_B}$
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
-20
-10
0
10
20
蒸発温度(℃)